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Thermodynamic study on complex of neodymium with glycine

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ABSTRACT

Neodymium complex with glycine, $Nd(Gly)_2Cl_3{\cdot}3H_2O$, was synthesized and characterized by IR spectra. The thermal stability of the complex was tested through TG and DTG and a possible mechanism of thermal decomposition was proposed. The heat capacities of the complex were measured by using an automated adiabatic calorimeter over the temperature range from $T = (80$ to $380)$ K, the thermodynamic functions, $[H_T - H_{298.15}]$ and $[S_T - S_{298.15}]$, were calculated based on the heat capacity measurements. Two (solid + solid) phase transitions in the ranges of $T = (170$ to $247)$ K were observed with the peak temperatures of 184.896 K and 231.217, respectively. The standard molar enthalpy of formation of $[Nd(Gly)_2Cl_3{\cdot}3H_2O]$ was determined to be (-3081.3 ± 1.1) kJ · mol^{-1} in terms of an isoperibol solution-reaction calorimeter.

1. Introduction

Rare earth elements have many unique properties and have been widely used in many areas, such as fertilizers, pesticides, antibacterial agents, and so on. As a result of such applications, rare earth elements are inevitably spread into the food chain and then into the bodies of human beings. Rare earth complexes with amino acids have been extensively studied because of their unique physiological and biochemical effects [1–3]. However, only a few reports are concerned with thermodynamic investigations [4–6].

As well known, the molar heat capacities $C_{p,m}$ of complex at different temperature are basic thermodynamic property data, from which many other thermodynamic properties such as enthalpy, entropy and Gibbs free energy that are important to theoretical and practical purposes, can be obtained [7,8]. Only with thermodynamic data of substances we can quantitatively describe their properties of energetics, such as thermal stability and stable states at different temperatures, melting point and energy change in different processes, and so on.

In the present work, a complex of neodymium chloride coordinated with glycine, $[Nd(Gly)_2Cl_3{\cdot}3H_2O]$ (Glycine abbreviated as Gly, Gly = NH_2CH_2COOH), was synthesized and characterized. A precision adiabatic calorimeter was used to investigate the low-temperature molar heat capacity ($C_{p,m}$) of the complex in the temperature range from (80 to 380) K. In accordance with Hess law, the standard molar enthalpy of formation for the complex was determined by using an isoperibolic solution reaction calorimeter with hydrochloric acid solution (2 mol · kg^{-1}) as a calorimetric solvent in terms of a proposed thermochemical cycle. The thermal stability of the compound was confirmed by differential scanning calorimetry (DSC) and thermogravimetric (TG) techniques.

2. Experimental

2.1. Sample preparation and characterization

The complex, $Nd(Gly)_2Cl_3{\cdot}3H_2O$, was synthesized according to the reported procedure [9]. Firstly, rare earth oxide (Neodymium oxide, Nd_2O_3) was dissolved in chloride acid to obtain the aqueous solution of the rare earth chloride. As follow, the aqueous solution was mixed with glycine in the molar ratio of 1:2 at about pH = 2.5 for 7 to 8 h. After that, the mixed solution was concentrated in a thermostat bath at $T = 323$ K until most of the water was evaporated slowly, then the concentrated solution was dried in a vacuum desiccator over phosphorus pentoxide for several weeks until lavender monocrystalline appeared. In the synthesis of the samples, the reagents are all of analytical grade. Information on the provenances and purities of the reagents used in the synthesis are listed in table 1.

The actual amount of C, H, and N in the as-prepared sample was confirmed by elemental analysis instrument (model PE-2400 II, USA). The contents of Cl and Nd were determined by EDTA titration and Mohr method, respectively. Found: C (10.66%), N (2.97%), H (2.49%), Cl (23.13%) and Nd (31.65%), which are close to the theoretical values of C (10.56%), N (3.08%), H (2.42%), Cl (23.39%)

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and Nd (31.72%). The formula of the complex was determined to be $Nd(Gly)_2Cl_3{\cdot}3H_2O$, and the purity obtained from the EDTA titration under the same conditions was found to be 99.78% (mass fraction), which was high enough to meet the requirements of the present calorimetric study. Infrared spectra of the complex $Nd(Gly)_2Cl_3{\cdot}3H_2O$, $Pr(Gly)_2Cl_3{\cdot}3H_2O$ [10], $Er(Gly)_2Cl_3{\cdot}3H_2O$ [11] and glycine were obtained from KBr pellets at room temperature using a IR spectrophotometer (model AVATAR 370 NICOLET USA).

Infrared spectra of $Nd(Gly)_2Cl_3{\cdot}3H_2O$, $Pr(Gly)_2Cl_3{\cdot}3H_2O$, $Er(Gly)_2Cl_3{\cdot}3H_2O$ and glycine are demonstrated in figure 1. Compared with the IR spectrum of glycine, the ν_s(carboxyl) band of $Nd(Gly)_2Cl_3{\cdot}3H_2O$ shifted from 1394 cm^{-1} to higher wavenumbers (1418 cm^{-1}), which reveals that the carboxyl groups of the ligand have been coordinated to the metal ion. The special absorption of NH_2 shifted from 3105 cm^{-1} to 3420 cm^{-1} (ν_{N-H}), from 2604 cm^{-1} to 2580 cm^{-1} (ν_{N-H}), and from 1500 cm^{-1} to 1477 cm^{-1} (υ_{NH_2}) indicates a hydrogen bond formed in the complex. A broad absorption band for ν_s (hydroxyl) appearing at 3400 cm^{-1} suggests the presence of water molecules in the complex. Meanwhile, it can be observed that the main diffraction peaks of $Nd(Gly)_2Cl_3{\cdot}3H_2O$ are in good agreement with that of $Pr(Gly)_2Cl_3{\cdot}3H_2O$ and $Er(Gly)_2Cl_3{\cdot}3H_2O$. The above results suggest that the structure of as-synthesized complex is similar to that of $Pr(Gly)_2Cl_3{\cdot}3H_2O$ and $Er(Gly)_2Cl_3{\cdot}3H_2O$.

A precision automatic adiabatic calorimeter was applied to measure the heat capacities of the complex. The principle and structure of the instrument have been described in detail elsewhere [12]. Briefly, the automatic adiabatic calorimeter is mainly composed of a sample cell, a miniature platinum resistance thermometer, an electric heater, the inner and outer adiabatic shields, two sets of six-junction chromel-constantan thermopiles installed between the calorimetric cell and the inner shield and between the inner and the outer shields, respectively, and a high vacuum can. The operating temperature ranges from T = (78 to 400) K; liquid nitrogen was used as the cooing medium. Prior to the heat capacity measurement of the sample, the molar heat capacities of the standard reference material α-Al_2O_3 (NIST, SRM 720) were measured from (78 to 400) K to verify the reliability of the adiabatic calorimeter. The results obtained in the calibration experiment showed that the deviations of calibration data obtained in this work from those of NIST were within ±0.3% over the whole temperature range, as compared with the recommended values reported by Archer [13] of NIST in the temperature range from (80 to 405) K.

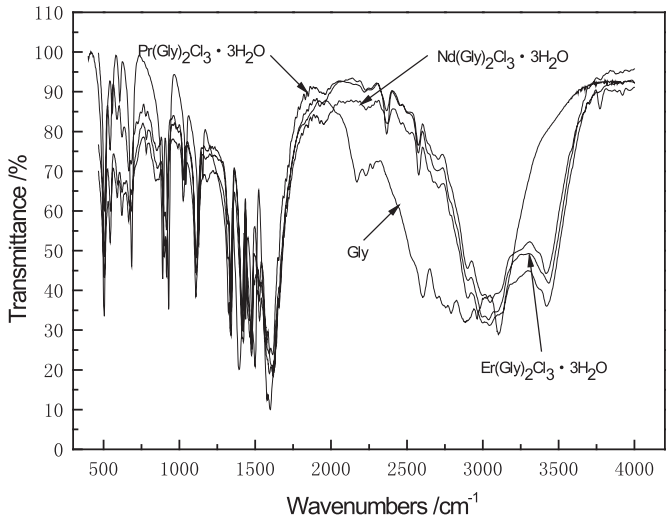

FIGURE 1. Infrared spectra of the complex $Nd(Gly)_2Cl_3{\cdot}3H_2O$, $Pr(Gly)_2Cl_3{\cdot}3H_2O$, $Er(Gly)_2Cl_3{\cdot}3H_2O$.

The heat capacity measurements were conducted by the standard procedure of intermittently heating the sample and alternately measuring the temperature. The heating rate and the temperature increments of the experimental points were generally controlled at 0.1 to 0.4 $K \cdot min^{-1}$ and at T = (1 to 4) K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were kept within 10^{-3} to 10^{-4} $K \cdot min^{-1}$ during the acquisition of heat capacity data. The mass of $Nd(Gly)_2Cl_3{\cdot}3H_2O$ used for the calorimetric measurements was 1.71636 g, which is equivalent to 0.003775 mol based on the molar mass of 454.73 $g \cdot mol^{-1}$.

2.2. DSC and TG measurements

Thermal analysis of $Nd(Gly)_2Cl_3{\cdot}3H_2O$ was performed using a differential scanning calorimeter (DSC-141, SETARAM, France) and a thermogravimetric analyzer (model DT-20B, Shimadzu, Japan). The DSC measurement was carried out with a heating rate of 10 $K \cdot min^{-1}$ under high-purity nitrogen with a flow rate of 50 $mL \cdot min^{-1}$. The mass of the sample used in the experiment was 3.36 mg. The calibrations for the temperature and heat flux of the calorimeter were performed prior to the experiment. The temperature scale was calibrated by measuring the melting points of Hg, In, Sn, Pb, and Zn at different heating rates, and the heat flux was calibrated using the Joule effect. Measurement of the melting temperature and the enthalpy of fusion of benzoic acid (NIST, SRM 39i) were carried out in this laboratory to check the accuracy of the instrument. The TG measurement of the complex was conducted at a heating rate of 10 $K \cdot min^{-1}$ under high-purity nitrogen with a flow rate of 120 $mL \cdot min^{-1}$. The mass of the sample used in the experiment was 9.47 mg. The reference crucible was filled with α-Al_2O_3. The TG-DTG equipment was calibrated by the thermal analysis of the SRM, $CaC_2O_4{\cdot}H_2O$(s).

2.3. Dissolution enthalpy measurements

The isoperibol solution reaction calorimeter (SCR-100, Wuhan University China) was applied to measure the dissolution enthalpies of the reactant and the product to obtain the formation enthalpies of the complex. The principle and structure of the instrument was described in detail elsewhere [14]. The calorimeter was tested by measuring the dissolution enthalpies of the KCl (calorimetric primary standard) in water at T = (298.15 ± 0.001) K. The mean dissolution enthalpy obtained from five experiments, is (17515 ± 12) $J \cdot mol^{-1}$, which is in conformity with the reported data (17536 ± 3.4) $J \cdot mol^{-1}$ [15].

The dissolution enthalpies of reactants and the products, and standard molar enthalpy of formation of $Nd(Gly)_2Cl_3{\cdot}3H_2O$ were determined through the proposed Hess thermochemical cycle [16], which is demonstrated in figure 2.

The dissolution enthalpy of H_2O (l), $\Delta_d H$, as one of the products in above cycle under the same condition was within the range of experimental error and may be omitted because the amount of H_2O (l) was very small according to the stoichiometric number of H_2O (l) in above cycle.

As illustrated in figure 2, the molar enthalpy of formation of $Nd(Gly)_2Cl_3{\cdot}3H_2O$(s) is given as:

$$\begin{aligned}\Delta_r H^{\theta}_m &= \Delta_f H^{\theta}_m[Nd(Gly)_2Cl_3 \cdot 3H_2O, s] + 3\Delta_f H^{\theta}_m(H_2O, l) \\ &\quad + \Delta_f H^{\theta}_m(NdCl_3 \cdot 6H_2O, s) + 2\Delta_f H^{\theta}_m(Gly, s) \\ &= \Delta s H_1 - \Delta s H_2 - \Delta_d H \approx \Delta s H_1 - \Delta s H_2, \end{aligned} \quad (1)$$

where $\Delta_f H^{\theta}_m$[$Nd(Gly)_2Cl_3{\cdot}3H_2O$,s], $\Delta_f H^{\theta}_m$($NdCl_3{\cdot}6H_2O$,s) and $\Delta_f H^{\theta}_m$(Gly,s) are the molar enthalpy of formation of the corresponding compounds. $\Delta_f H^{\theta}_m$[$Nd(Gly)_2Cl_3{\cdot}3H_2O$,s] could be calculated from the following equation: